

“On the Intimate Structure of Crystals. Part III. Crystals of the Cubic System with Cubic Cleavage.” By W. J. SOLLAS, LL.D., D.Sc., F.R.S., Professor of Geology in the University of Oxford. Received March 8,—Read March 17, 1898.

The remaining metals and diatomic compounds which crystallise in the cubic system and possess cubic cleavage are few in number; some of them form the subject of the present communication. Triatomic compounds fulfilling these conditions are left for later consideration.

Ammonium chloride.—M. w., 53·506; sp. gr., 1·52 (Schröder); m. v., 35·201. Volume of four molecules, $35\cdot2 \times 4 = 140\cdot8$.

Edge of cubelet, or sum of the diameters of one molecule of NH_4 and one atom of Cl., $\frac{3}{4}140\cdot8 \dots\dots\dots 5\cdot204$

Diameter of one atom of Cl. 2·4954
 „ „ NH_4 2·7134

Gross volume of NH_4 , $2\cdot7134^3 = 19\cdot98$; volume of molecular sphere of NH_4 , $19\cdot98 \times \frac{1}{6}\pi = 10\cdot46$.

Galena, PbS .—M. w., 238·97; sp. gr., 7·25 to 7·77 (7·513 taken); m. v., 31·78; volume of four molecules, $31\cdot78 \times 4 = 127\cdot12$.

Edge of cubelet or diameter of $\text{Pb} + \text{S} \dots \dots 5\cdot028$

Diameter of one atom of Pb 2·625
 „ „ S 2·408

Lead enters into combination without change of volume. Gross atomic volume of Pb, $2\cdot625^3 = 18\cdot1$; volume of atomic sphere, $18\cdot1 \times \frac{1}{6}\pi = 9\cdot481$. Gross volume of S, $2\cdot408^3 = 13\cdot96$.

Lead selenide, PbSe .—M. w., 286·01; sp. gr., 8·154 (Little); m. v., 35·076. Volume of four molecules, $35\cdot076 \times 4 = 140\cdot305$.

Edge of cubelet or diameter of $\text{Pb} + \text{Se} \dots \dots 5\cdot1962$

Diameter of one atom of Pb 2·625
 „ „ Se 2·571

Gross volume of Se, 17·0; volume of atomic sphere, 8·9.

Of the oxides which crystallise in the cubic system with cubic cleavage only three are sufficiently well known to afford data for

treatment; these are calcium, magnesium, and stannous oxides. The metals calcium and magnesium undergo a considerable amount of condensation on entering into combination; it will therefore be more convenient to select stannous oxide as the compound which is to serve as the basis for obtaining the relative diameter of oxygen; but this course is not without its disadvantages, for very different values have been found by different experimenters for the specific gravity of stannous oxide, and the same is true of the metal tin itself, which further has the additional defect of crystallising, not in the cubic, but in the tetragonal system.

Tin.—At. w., 118.1; sp. gr., 7.0 to 7.5; mean, 7.25 (taken).

Gross atomic volume, 16.29; volume of atomic sphere, 8.53.

Diameter of atom, 2.535.

Stannous Oxide, SnO .—M. w., 134.1; sp. gr., 6.1 (Nordenskjöld), 6.6 at 0°C . (Berzelius, Ditte). The latter value is taken.

M. v., 20.313. Volume of four molecules, 81.273.

Edge of cubelet or diameter of SnO	4.3316
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Diameter of one atom of Sn	2.535
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" " O	1.8508
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Gross volume of oxygen, 6.34; volume of atomic sphere, 3.32.

Calcium oxide, CaO .—M. w., 56; sp. gr., 3.251; m. v., 17.25.

Volume of four molecules, $17.25 \times 4 = 68.9$.

Edge of cubelet or diameter of CaO	4.100
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Diameter of one atom of O	1.851
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" " Ca	2.27
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Gross volume of Ca , 11.695. The gross volume of Ca in the metallic state is 25.48.

Periclase, MgO .—M. w., 40.38; sp. gr., 3.636; m. v., 11.105.

Volume of four molecules, 44.423.

Edge of cubelet or diameter of MgO	3.5416
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Diameter of one atom of O	1.851
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" " Mg	1.6936
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Gross volume of Mg , 4.858. The gross volume of Mg in the metallic state is 14.341. It crystallises in the hexagonal system. These results are more or less uncertain; it must be borne in mind that the volume of oxygen differs greatly in different compounds.

The metals which remain for consideration in the present communication are as follows:—

Copper.—At. w., 63·8; sp. gr., 8·945; at. v., 7·0766. Volume of atomic sphere, 3·7053; diameter, 1·92.

Gold.—At. w., 197·2; sp. gr., 19·33 at 17·5°; at. v., 10·202. Diameter of atomic sphere, 2·169.

Iron.—At. w., 56; sp. gr., 7·85 at 16° (Caron); at. v., 7·134. Diameter of atomic sphere, 1·925; or sp. gr. 8·139 (Roberts Austen); at. v., 6·88; diameter of atomic sphere, 1·902.

Manganese.—At. w., 55; sp. gr., 7·3921 at 22°; at. v., 7·44. Diameter of atomic sphere, 1·952.

Platinum.—At. w., 194·8; sp. gr., 21·5 at 17·6°; at. v., 9·0605. Diameter of atomic sphere, 2·085.

Palladium.—At. w., 106; sp. gr., 11·4 at 22·5°; at. v., 9·2983. Diameter of atomic sphere, 2·103.

The Absorption of Hydrogen by Palladium.—Strong confirmatory evidence of the existence of the open packing which we have assigned to the metals crystallising in the cubic system is afforded by the phenomenon of solid solution (so called), and particularly by the absorption of hydrogen by palladium. When similar spheres are arranged in open cubic order, they form straight rows in contact, running parallel to the edges of the cube they constitute, and corresponding to these files of spheres are open galleries, lying between and running parallel with them. Through these galleries atoms, if small enough, might pass from end to end without encountering any obstacle, and thus the transpiration of hydrogen through metallic plates might be explained. Further, between every set of eight atoms, forming a primitive cube of the pile, the gallery widens out into a chamber, in which an atom smaller than that of the metal might conceivably lodge. The diameter of an atom which could occupy the space between eight atoms, forming a primitive cube, of palladium, can readily be calculated. The diameter of an atom of palladium has already been determined to be 2·103, the edge of a cubelet formed of eight atoms is therefore 4·206, and the length of the trigonal axis of such a cube is $4·206 \times \sqrt{3} = 7·285$; and $(7·285 - 4·206)/2 = 1·538$, the length of the diameter of an atom, which would just occupy the central space. This estimate, however, requires modification, by virtue of the fact that palladium progressively increases in volume as the absorption of hydrogen takes place. In Dewar's determinations the expansion was measured by the change produced in the specific gravity of the palladium; the lowest specific gravity which Dewar observed was 10·8033; this gives for the edge of the primitive cube a value of 4·2818. Assuming that the atoms of palladium have not increased in volume by absorbing energy, but have simply become more remote from one another, we may proceed as follows: $4·2818 \times \sqrt{3} = 7·416$, the length of the tri-

gonal axis of the primitive cube, and thus $(7.416 - 4.206)/2 = 1.605$, the true diameter of an atom which could just occupy the central interspace of the primitive cubelet. The cube of this number will give us the gross volume of the atom of occluded hydrogen; it is 4.134. If now we turn to Rücker's address on "The Range of Molecular Forces,"* we find the most probable estimates given for the volume of hydrogen (H) are as follows:—From K (Boltzman) 4.4, (Klemenčić) 4.4; from *n* (Mascart) 4.65; from *b* (Van der Waals and O. Meyer) 4.4. Between these numbers and that we have just obtained there is a very remarkable concordance.

It may further be observed that the number of such interspaces as we have considered is, to the number of atoms among which they lie, in the ratio of 1 : 1, so that from purely geometrical considerations it might be inferred that the limiting value for the absorption of hydrogen by palladium would be reached with the formation of the substance Pd_2H_2 . Observation shows that this limit is never exceeded, never even attained, while that which is reached may fairly be represented by the formula Pd_3H_2 . It is obvious that purely geometrical considerations are not all that are involved, and to discuss other factors would be to trespass beyond our province. There is one point in direct connection with our inquiry which must not, however, be disregarded. The value we have found for the diameter of hydrogen was obtained on the assumption that all the central spaces were occupied by hydrogen, which would only be the case if Pd_2H_2 were formed; the observed ratio, Pd_3H_2 , would lead us to believe that only two-thirds of the spaces are so occupied. This renders necessary a correction in our estimate, which would slightly increase the dimensions of the hydrogen atom. It is not possible, however, to introduce this correction, on account of the absence of information regarding the crystalline form assumed by Pd_3H_2 . If crystals of palladium be capable of taking a charge of hydrogen, there should be no difficulty in ascertaining whether a change in crystalline form accompanies occlusion. On the assumption that the maximum expansion of palladium due to occlusion is confined to two-thirds of the volume of the metal experimented upon, I find that the diameter of the hydrogen atom should be 4.395. Possibly the assumption is not defensible, but in any case it would appear that the amount of coincidence we have already obtained between the dimensions of the hydrogen atom, as calculated from the crystalline structure we have assigned to palladium (along with other metals) and the dimensions which follow from other modes of inquiry, affords strong confirmation of our hypothesis.

The absorption of hydrogen by potassium might easily take place without producing any marked expansion, *i.e.*, so far as the relative

* 'Trans. Chem. Soc.,' vol. 63, p. 257, 1888.

dimensions of the atoms are concerned in the matter, for the interspace in the centre of a primitive cube of potassium is large enough to house an atom of a gross volume exceeding 17.

In the case of iron the central space is notably smaller than in that of palladium; supposing no expansion to occur on absorption, the largest atom it could contain would have a diameter of 1.392, corresponding to a volume of 2.697.

It is probable, however, that a change in crystalline system is associated with the absorption of gases by iron and nickel. This is suggested by the curious effect produced on the nature of these metals by repeated absorption of hydrogen, at least in the case of nickel, which loses its cohesion and after repeated treatment becomes converted into a friable powder.

The galleries formed by ranges of central spaces present constrictions at intervals corresponding to the places where the four spheres forming the face of a cubelet are most closely approximate; the ratio of the diameter of a sphere that could just traverse one of these constrictions is to that of a sphere which would just occupy a central space as $\sqrt{2} : \sqrt{3}$. Hence the passage of an atom into the central chamber involves either a displacement of the atoms surrounding the entrance or a contraction in the volume of the entering guest. Is it possible that the "singing" of palladium, which accompanies the process of occlusion, is connected with vibratory movements of its atoms as they open and close the entrances to the central chambers?

In conclusion it may be pointed out that all the metals which are known to occlude hydrogen, viz., potassium, sodium, magnesium, iron, nickel, platinum, and palladium, are paramagnetic, sodium and magnesium being the only cases of an uncertain nature, while lead and gold, which offer roomy central spaces for the occupation of hydrogen, but do not absorb it, are diamagnetic.

"The Electrical Response of Nerve to a Single Stimulus investigated with the Capillary Electrometer. Preliminary Communication." By F. GOTCH, M.A., F.R.S., Professor of Physiology, University of Oxford, and G. J. BURCH, M.A. (Oxon). Received April 1,—Read May 12, 1898.

The electrical changes which are evoked in nerve by a single stimulus have up to the present been but little investigated. The examination of the phenomena has been almost entirely limited to observations upon the galvanometric deflections caused by the summed effects of a rapid succession of excitations, and rheotome methods,